UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

FABRICATION AND CHARACTERIZATION OF HIGH PERFORMANCE ELECTROCHEMICAL CAPACITOR USING VERTICALLY ALIGNED CARBON NANOTUBE DIRECT GROWTH TECHNIQUE

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A thesis submitted
in fulfillment of the requirements for the degree of Master of Science
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DECLARATION

I declare that this thesis entitled "Fabrication and Characterization of High Performance Electrochemical Capacitor Using Vertically Aligned Carbon Nanotube Direct Growth Technique" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....

Name : NOR SYAFIRA BINTI ABDUL MANAF

Date :

APPROVAL

I hereby declare that I have read this dissertation/report and in my opinion this dissertation/report is sufficient in terms of scope and quality as a partial fulfillment of Master of Science in Manufacturing Engineering.

Signature :………………..

Supervisor Name : DR. MOHD ASYADI AZAM BIN MOHD ABID

Date :

DEDICATION

Special dedicated to my beloved parents

Abdul Manaf Bin Omar & Shamsiah Binti Mohd Yunus

My family

Muhammad Rozif Bin Roslan

Muhamad Shahril Bin Abdul Manaf

Muhamad Shahrizal Bin Abdul Manaf

Muhamad Shahairul Bin Abdul Manaf

And to all my relatives and friends for their supports, courage and prayers.

May Allah SWT bless all of you.

ABSTRACT

Increasing demand for energy requirement has attracted considerable attention among researchers to develop efficient energy storage device. Among energy storage devices, electrochemical capacitor (EC) has great potential for its capability to deliver more power than batteries and store more energy than conventional capacitors. The electrode preparation technique is the most crucial factor to be considered towards development high performance ECs. In this research, vertically aligned carbon nanotubes (VACNTs) were directly grown on conducting foil using alcohol catalytic chemical vapour deposition (ACCVD) technique and act as electrode for ECs. This technique would be enhanced the capacitance performance due to direct electrical contact between VACNTs and conducting foils. Also, this one simple technique can reduce the fabrication complexity and number of processes. Binder material which normally insulating is not incorporated in the device structure, thus could decrease internal resistance and give good effect on capacitance performance. The VACNT electrode was characterized using Raman spectroscopy and electron microscopies for growth confirmation and for quality level investigation. Electrochemical analysis was performed by using cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. A maximum of 206 F g^{-1} specific gravimetric capacitance (C_{sp}) was obtained from the heat treated VACNTs electrode in 1M $LiPF_6$ electrolyte, which suggests that the VACNTs could be an excellent candidate as the electrode in ECs. This EC also have good rate capability for industrial usage, and good response performance with low resistance value from the impedance analysis. Small IR drop results from galvanostatic charge discharge analysis indicates low resistance and high power characteristic

ABSTRAK

Peningkatan dalam keperluan tenaga telah menarik perhatian ramai penyelidik untuk memajukan penggunaan alat penyimpan tenaga secara efektif. Dikalangan semua jenis alat penyimpan tenaga, kapasitor elekrokimia mempunyai potensi untuk memberikan lebih kuasa berbanding bateri dan menyimpan lebih tenaga daripada kapasitor biasa. Kaedah penyediaan electrod merupakan faktor penting dalam memajukan prestasi kapasitor elektrokimia. Dalam penyelidikan ini, nano tiub karbon tegak sejajar telah ditumbuhkan terus di atas konduktif substrat melalui teknik alkohol pemangkin pemendapan wap kimia dan digunakan sebagai elektrod dalam kapasitor elekrokimia. Kaedah ini dapat meningkatkan prestasi kapasitans kerana pegaliran terus elektrik diantara nano tiub karbon tegak sejajar dan substrat konduktif. Kaedah ini juga mudah dan boleh mengurangkan kesusahan dan langkah-langkah dalam penyediaan elektrod. Bahan pengikat yang mempunyai sifat penebat tidak digunakan dalam teknik ini kerana ia akan menyebabkan peningkatan rintangan dalaman, Oleh itu, rintangan dalaman dapat dikurangkan tanpa penggunaan bahan pengikat dan memberi kesan baik kepada prestasi kapasitans. Pengesahan rupa pertumbuhan dan kualiti nano tiub karbon tegak sejajar elektrod dilihat dan dianalisa menggunakan spectroskopi Raman dan mikroskopi elektron. Elekrokimia analisis telah dijalankan dengan menggunakan voltammetri kitaran, galvanostatik cas dan nyahcas, dan spektroskopi impedans elecktrokimia. Nilai maksima spesifik gravimetrik kapasitans yang didapati adalah 206 F g^{-1} *daripada haba terawat nano tiub karbon tegak sejajar dalam 1M* $LiPF_6$ *elektrolit dimana ini menunjukkan nano tiub karbon tegak sejajar calon yang terbaik untuk digunakan sebagai elektrod pada kapasitor elekrokimia. Kapasitor elekrokimia ini juga menunjukkan kadar kemampuan yang baik untuk penggunaan di industri dan juga memberi prestasi respon yang terbaik dengan pengurangan nilai rintangan dalaman daripada analisis impedans. Kejatuhan voltan yang kecil daripada analisis cas dan nyahcas juga membuktikan rintangan dalaman yang kecil dan kapasitor elektrokimia ini mempunyai sifat kuasa yang tinggi.*

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LIST OF ABBREVIATIONS

AC	Activated Carbon
ACCVD	Alcohol Catalytic Chemical Vapour Deposition
AG-VACNT	As-Grown Vertically Aligned Carbon Nanotube
CNT	Carbon Nanotube
CV	Cyclic Voltammetry
CVD	Chemical Vapour Deposition
DMC	Dimethyl Carbonate
EC	Electrochemical Capacitor
EDLC	Electrochemical Double Layer Capacitor
EIS	Electrochemical Impedance Spectroscopy
ESR	Equivalent Series Resistance
FESEM	Field Emission Scanning Electron Microscopy
GPE	Gel Polymer Electrolyte
HT-VACNT	Heat-Treated Vertically Aligned Carbon Nanotube
MWCNT	Multi Wall Carbon Nanotube
PVD	Physical Vapour Depostion
RF	Radio Frequency
SCE	Saturated Calomel Electrode
SEI	Solid Electrolyte Interface
SPE	Solid Polymer Electrolyte
SWCNT	Single Wall Carbon Nanotube

TEM	Transmission Electron Microscopy
VACNT	Vertically Aligned Carbon Nanotube

LIST OF SYMBOLS

µm	-	Micrometre
A	-	Ampere
Ag/AgCl	-	Silver/Silver Chloride
Al	-	Aluminium
Al_2O_3	-	Aluminium Oxide
Ar	-	Argon
Co	-	Cobalt
C_{sp}	-	Specific Capacitance
d	-	EDLC thickness
EB-	-	Electron Beam
F g^{-1}	-	Farad per Gram
Fe	-	Iron
Fe_3O_4	-	Iron(III) Oxide
g	-	Gram
H_2	-	Hydrogen
Hg/HgO	-	Mercury/Mecury Oxide
Hz	-	Frequency
I	-	Current
m	-	Mass
min	-	Minute
mm	-	Millimetre

$mV\ s^{-1}$	-	Voltage Scan Rate
N_2	-	Nitrogen
Ni	-	Nickel
NiO	-	Nickel Oxide
nm	-	Nanometer
O_2	-	Oksigen
ºC	-	Celsius Degree
Pa	-	Pascal
qa	-	Anodic Voltammetric Charge
qc	-	Cathodic Voltammetric Charge
Rs	-	Equivalent Series Resistance
RuO_2	-	Ruthenium Oxide
s	-	Second
S	-	Surface Area of Electrode/Electrolyte Interface
sccm	-	Standard Centimetre Per Cubic
V	-	Voltage
$W\ kg^{-1}$	-	Power Density
$Wh\ kg^{-1}$	-	Energy Density
Z'	-	Real Impedance
Z"	-	Imaginary Impedance
ε	-	Permittivity or Dielectric Constant
Ω	-	Ohm

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CHAPTER 1

INTRODUCTION

1.1 Background

In today‟s world, global warming problem and limited availability of non-renewable resources from fossil fuels such as coal, crude oil, and natural gas have urged the world to move towards development of more sustainable energy sources. Renewable resources such as solar and wind power become alternative source that have their ability to generate electricity (Li and Wei, 2013). However, these kinds of sources face a number of additional challenges and restrictions for energy consumption due to solar and wind power only generate electricity when the sun is shining or the wind is blowing, whereas continuous utilization of energy must be up to 24 h a day (Abruña et al., 2008). As global energy consumption rise dramatically due to the increase in population and higher living standards, development of improved methods is necessary for storing electricity when it is available and retrieving when it is needed (Shukla et al., 2000).

Energy storage devices are introduced to overcome the limitation of using renewable source. There are a lot of researchers try to develop more efficient energy storage system that is low-cost, environmentally friendly with better performance to meet the market requirement (Huang et al., 2012). There are several types of devices for newly electrochemical energy storage and conversion such as batteries, fuel cells, conventional capacitors, and electrochemical capacitors (ECs). They can store energy in various forms such as electrochemical, kinetic, pressure, potential, electromagnetic, chemical, and thermal. The energy storage devices can be used in various fields such as transportation and consumer electronics. (Pollet et al., 2012; Winter et al., 2004). Among those devices, ECs have attracted a great worldwide research attention because of their potential applications. It exhibits great properties as energy storage devices (Zhang et al., 2009). At present, the markets of ECs have been developed very drastically because the increasing demand from customers for various applications including electric vehicle, mobile phone and a lap top computer, and so on. In addition, the consideration on environmental pollution is important factor in technology‟s development and here ECs have been interested as a clean energy technology (Endo et al., 2001).

ECs also known as electrochemical double layer capacitors (EDLC), supercapacitors, ultracapacitors, pseudocapacitors, power capacitors, gold capacitors or power cache (Zhang et al., 2009). They have capability to store electrical charge in various applications such as transportations (e.g., hybrid electric vehicles, metro trains and tramways), automotives (e.g., electrical power steering), and consumer electronics (e.g., laptops, cell phones, and video cameras) (Simon and Gogotsi, 2010). Today several companies such as Maxwell, Panasonic, Cooper, AVX, Cap XX, ELNA, ESMA, and several others have involved in the development of ECs (Li et al., 2012). Currently, ECs fill in the gap between batteries and conventional capacitors in term of energy density and power density, respectively. As compared with among energy storage devices, there are many advantages of ECs including high power density, long life cycle, fast charge-discharge rate, large thermal operating range, light, flexible packaging, and low maintenance (Hsieh et al., 2012; Obreja, 2008).

ECs consist of two electrodes immersed in an electrolyte with a dielectric separator between the electrodes (Pan et al., 2010). The electrodes or active materials